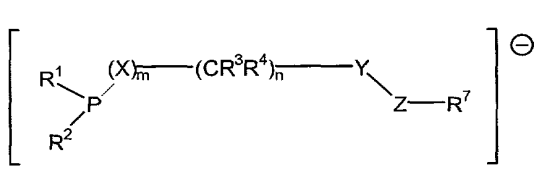
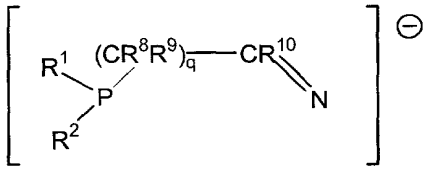
CLAIMS

What is claimed is:

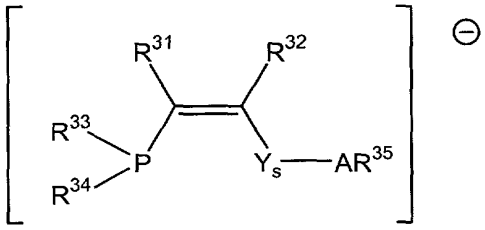
1. A process for the polymerization of olefins, comprising the step of contacting, at a temperature of about -100°C to about +200°C, at least one polymerizable olefin with an active polymerization catalyst comprising a Group 3 through 11 (IUPAC) transition metal or a lanthanide metal complex of a ligand of the formula (I), (II) or (XII)



(I)



(II)



(XII)

wherein:

R^1 and R^2 are each independently hydrocarbyl, substituted hydrocarbyl or a functional group;

Y is $CR^{11}R^{12}$, S(T), $S(T)_2$, P(T)Q, NR^{36} or $NR^{36}NR^{36}$;

X is O, CR^5R^6 or NR^5;

A is O, S, Se, N, P or As;

Z is O, Se, N, P or As;

each Q is independently hydrocarbyl or substituted hydrocarbyl;

R^3, R^4, R^5, R^6, R^{11} and R^{12} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^7 is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when Z is O or Se, R^7 is not present;

R^8 and R^9 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{10} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

each T is independently =O or $=NR^{30}$;

R^{30} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{33} and R^{34} are each independently hydrocarbyl or substituted hydrocarbyl, provided that each is independently an aryl substituted in at least one position vicinal to the free bond of the aryl group, or each independently has an E_s of -1.0 or less;

R^{35} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when A is O, S or Se, R^{35} is not present;

each R^{36} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

m is 0 or 1;

s is 0 or 1;

n is 0 or 1; and

q is 0 or 1;

and provided that:

any two of R^3, R^4, R^5, R^6, R^8, R^9, R^{11} and R^{12} bonded to the same carbon atom taken together may form a functional group;

any two of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{11}, R^{12}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} and R^{36} bonded to the same atom or vicinal to one another taken together may form a ring; and

when said ligand is (I), Y is C(O), Z is O, and R^1 and R^2 are each independently hydrocarbyl, then R^1 and R^2 are each independently an aryl substituted in one position vici-

nal to the free bond of the aryl group, or R^1 and R^2 each independently have an E_s of -1.0 or less.

2. The process of claim 1, wherein said transition metal is Ni, Pd, Pt, Fe, Co, Ti, Zr, V, Hf, Cr or Cu.

3. The process of claim 2, wherein said transition metal is Ni, Pd, Ti or Zr.

4. The process of claim 1, wherein the ligand is (I) and:

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

the transition metal is Ti, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

the transition metal is Zr, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, R^7 is hydrocarbyl or substituted hydrocarbyl, Y is $CR^{11}R^{12}$, R^{11} is hydrogen, R^{12} is hydrocarbyl or substituted hydrocarbyl, and Z is N; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are oxo, and Z is O; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, R^7 is hydrocarbyl or substituted hydrocarbyl, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are oxo, and Z is N; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O and Z is O; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =N-silyl, Z is N and R^7 is silyl; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O, Z is N, and R^7 is hydrocarbyl or substituted hydrocarbyl; or

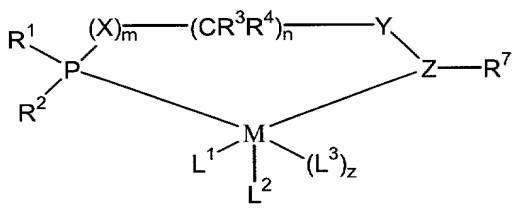
the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are a ring and Z is O; or

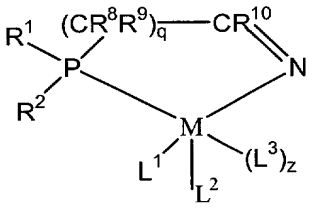
the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are N-hydrocarbyl- or N-substituted hydrocarbylimino, Z is N and R^7 is hydrocarbyl or substituted hydrocarbyl; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O and Z is O; or

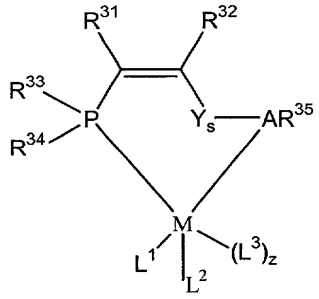
the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are sulfo, Z is N and R^7 is hydrocarbyl or substituted hydrocarbyl.

5. A process for the polymerization of olefins, comprising the step of contacting, at a temperature of about -100°C to about +200°C, at least one polymerizable olefin with a compound of the formula (IV), (V) or (XIII)





(IV) (V)



(XIII)

wherein:

R^1 and R^2 are each independently hydrocarbyl, substituted hydrocarbyl or a functional group;

Y is $CR^{11}R^{12}$, S(T), $S(T)_2$, P(T)Q, NR^{36} or $NR^{36}NR^{36}$;

X is O, CR^5R^6 or NR^5;

A is O, S, Se, N, P or As;

Z is O, Se, N, P or As;

each Q is independently hydrocarbyl or substituted hydrocarbyl;

R^3, R^4, R^5, R^6, R^{11} and R^{12} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^7 is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when Z is O or Se, R^7 is not present;

R^8 and R^9 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{10} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

each T is independently =O or $=NR^{30}$;

R^{30} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{33} and R^{34} are each independently hydrocarbyl or substituted hydrocarbyl, provided that each is independently an aryl substituted in at least one position vicinal to the free bond of the aryl group, or each independently has an E_s of -1.0 or less;

R^{35} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when A is O, S or Se, R^{35} is not present;

each R^{36} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

m is 0 or 1;

s is 0 or 1;

n is 0 or 1; and

q is 0 or 1;

M is a Group 3 through Group 11 transition metal or a lanthanide metal; and

L^1 is a monodentate monoanionic ligand into which an ethylene molecule may insert between L^1 and M, and L^2 is a monodentate neutral ligand which may be displaced by ethylene or an empty coordination site, or L^1 and L^2 taken together are a monoanionic bidentate ligand into which ethylene may insert between said monoanionic bidentate ligand and said nickel atom, and each L^3 is independently a monoanionic ligand and z is the oxidation state of M minus 2;

and provided that;

any two of R^3, R^4, R^5, R^6, R^8, R^9, R^{11} and R^{12} bonded to the same carbon atom taken together may form a functional group;

any two of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{11}, R^{12}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} and R^{36} bonded to the same atom or vicinal to one another taken together may form a ring; and

when said compound is (IV), Y is C(O), Z is O, and R^1 and R^2 are each independently hydrocarbyl, then R^1 and R^2 are

each independently an aryl substituted in one position vicinal to the free bond of the aryl group, or R^1 and R^2 each independently have an E_s of -1.0 or less.

6. The process of claim 5, wherein M is Ni, Pd, Pt, Fe, Co, Ti, Zr, V, Hf, Cr or Cu.

7. The process of claim 6, wherein M is Ni, Pd, Ti or Zr.

8. The process of claim 5, wherein the compound is (IV) and:

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

M is Ti, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

M is Zr, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} is hydrocarbyl or substituted hydrocarbyl, R^{12} is hydrocarbyl, substituted hydrocarbyl or a functional group, and Z is O; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, R^7 is hydrocarbyl or substituted hydrocarbyl, Y is $CR^{11}R^{12}$, R^{11} is hydrogen, R^{12} is hydrocarbyl or substituted hydrocarbyl, and Z is N; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are oxo, and Z is O; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, R^7 is hydrocarbyl or substituted hydrocarbyl, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are oxo, and Z is N; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O and Z is O; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =N-silyl, Z is N and R^7 is silyl; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O, Z is N, and R^7 is hydrocarbyl or substituted hydrocarbyl; or

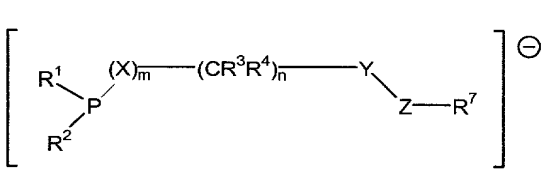
M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are a ring and Z is O; or

M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are N-hydrocarbyl- or N-substituted hydrocarbylimino, Z is N and R^7 is hydrocarbyl or substituted hydrocarbyl; or

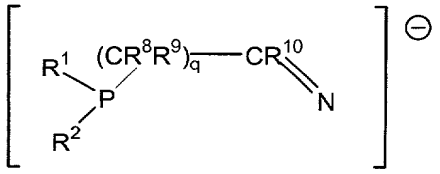
M is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is S(T), T is =O and Z is O; or

the transition metal is Ni, m is 0, n is 1, R^3 and R^4 are hydrogen, Y is $CR^{11}R^{12}$, R^{11} and R^{12} taken together are sulfo, Z is N and R^7 is hydrocarbyl or substituted hydrocarbyl.

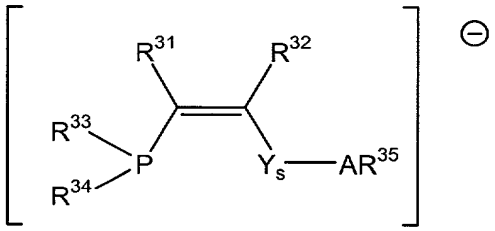
9. A polymerization catalyst component comprising a Group 3 through 11 transition metal or lanthanide metal complex of a ligand of the formula



or



(I) (II)



(XII)

wherein:

R^1 and R^2 are each independently hydrocarbyl, substituted hydrocarbyl or a functional group;

Y is $CR^{11}R^{12}$, S(T), $S(T)_2$, P(T)Q, NR^{36} or $NR^{36}NR^{36}$;

X is O, CR^5R^6 or NR^5;

A is O, S, Se, N, P or As;

Z is O, Se, N, P or As;

each Q is independently hydrocarbyl or substituted hydrocarbyl;

R^3, R^4, R^5, R^6, R^{11} and R^{12} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^7 is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when Z is O or Se, R^7 is not present;

R^8 and R^9 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{10} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

each T is independently =O or $=NR^{30}$;

R^{30} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{33} and R^{34} are each independently hydrocarbyl or substituted hydrocarbyl, provided that each is independently an aryl substituted in at least one position vicinal to the free bond of the aryl group, or each independently has an E_s of -1.0 or less;

R^{35} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that when A is O, S or Se, R^{35} is not present;

each R^{36} is independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

m is 0 or 1;

s is 0 or 1;

n is 0 or 1; and

q is 0 or 1;

and provided that:

any two of R^3, R^4, R^5, R^6, R^8, R^9, R^{11} and R^{12} bonded to the same carbon atom taken together may form a functional group;

any two of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{11}, R^{12}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} and R^{36} bonded to the same atom or vicinal to one another taken together may form a ring; and

when said ligand is (I), Y is C(O), Z is O, and R^1 and R^2 are each independently hydrocarbyl, then R^1 and R^2 are each independently an aryl substituted in one position vicinal to the free bond of the aryl group, or R^1 and R^2 each independently have an E_s of -1.0 or less.

10. The component of claim 9, which is on a solid support.

11. The component of claim 9, wherein a cocatalyst which is an alkylaluminum compound or a borane or both is also present.

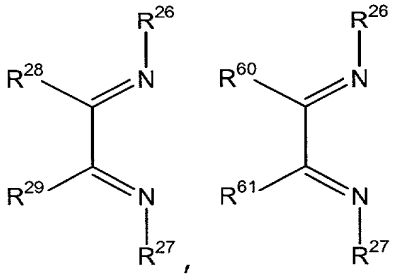
12. A process for forming an ethylene/polar monomer copolymer, comprising the step of contacting, under polymerizing conditions, a nickel complex of a bidentate neutral ligand or a bidentate monoanionic ligand, with a monomer component comprising one or more hydrocarbon olefins and one or more polar comonomers (and other optional components such as, for example, one or more cocatalysts and/or other addi-

tives), at a temperature of about 60°C to about 170°C, provided that when CO is present, at least one other polar monomer is present.

13. The process of claim 12, wherein ethylene is present and an ethylene partial pressure of at least about 0.67 MPa is used.

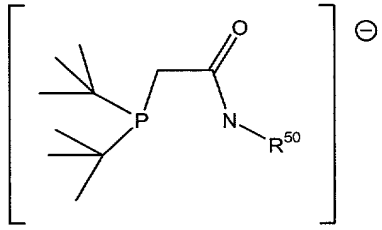
14. The process of claim 12, wherein said one or more polar comonomers comprises $H_2C=CHR^{20}C(O)Y$, or $H_2C=CR^{25}C(O)Y$, wherein R^{20} is alkylene or substituted alkylene, R^{25} is hydrogen, and Y is -OH, $-NR^{21}R^{22}$, $-OR^{23}$, or $-SR^{24}$, wherein R^{21} and R^{22} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, R^{23} and R^{24} are each hydrocarbyl or substituted hydrocarbyl.

15. The process of claim 12, wherein said bidentate ligand is

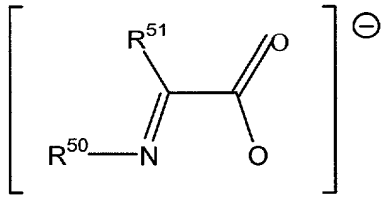


(XIV)

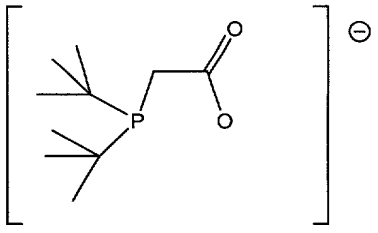
(XV)



(XVI)



(XVII)



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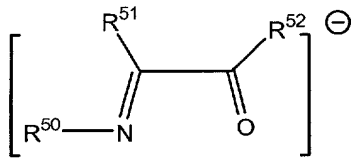

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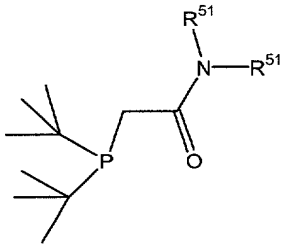
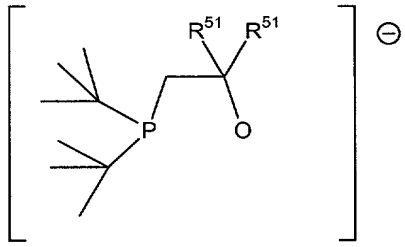


(XX)

or



(XXI)

wherein:

R^{26} and R^{27} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^{28} and R^{29} taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

R^{60} and R^{61} are each independently functional groups bound to the rest of (XV) through heteroatoms (for example O, S or N), or R^{60} and R^{61} (still containing their heteroatoms) taken together form a ring.

each R^{50} is independently hydrocarbyl or substituted hydrocarbyl;

each R^{51} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

each R^{52} is hydrocarbyl, substituted hydrocarbyl, hydrocarbyloxy, or substituted hydrocarbyloxy.

16. A polymer, consisting essentially of repeat units derived from ethylene, and one or more polar olefins of the formula $H_2C=CHC(O)R^{32}$, wherein R^{32} is $-OR^{34}$ or any group readily derivable from it, and R^{34} is hydrocarbyl or substituted hydrocarbyl, wherein:

said polymer contains "first branches" of the formula $-(CH_2)_nCH_3$ and "second branches" of the formula $-(CH_2)_mC(O)R^{32}$, wherein m and n are independently zero or an integer of 1 or more; and

said polymer has the following structural characteristics:

(a) one or both of:

(1) the ratio of first branches wherein n is 0 to first branches wherein n is 1 is about 3.0 or more; and

(2) the ratio of first branches wherein n is 0 to first branches wherein n is 3 is 1.0 or more; and

(b) one or both of:

(1) the total number of first branches in which n is 0, 1, 2 and 3 in said polymer is about 10 or more per 1000 CH_2 groups; and

(2) the incorporation of repeat units derived from $H_2C=CHC(O)R^{32}$ is 0.3 mole percent or more based on the total repeat units derived from the hydrocarbonolefin and $H_2C=CHC(O)R^{32}$.

17. A polymer, consisting essentially of repeat units derived from:

one or more hydrocarbon olefins, such as ethylene, and

one or more polar olefins of the formula $H_2C=CHC(O)R^{32}$, wherein R^{32} is $-OR^{34}$, or any group readily derivable from it, and R^{34} is hydrocarbyl or substituted hydrocarbyl;

wherein in said polymer incorporation of repeat units derived from $H_2C=CHC(O)R^{32}$ is 0.3 mole percent or more based on the total repeat units; and

wherein said polymer has one or both of the following structural characteristics:

at least 5 mole percent of said repeat units derived from $H_2C=CHC(O)R^{32}$ are present in said polymer as end groups; and

said end groups are at least 0.001 mole percent of the total repeat units in said polymer;

and provided that said end groups have the formula

$$\sim\sim\sim\sim\sim\sim\sim\sim\text{-}HC=CH\text{-}C(O)\text{-}R^{32}$$

wherein ~~~~~~~ is the remainder of the polymer chain of said end group.

18. A polymer, consisting essentially of:

repeat units derived from ethylene;

repeat units derived from one or more monomers of the formula $H_2C=CHC(O)R^{32}$, wherein each R^{32} is independently $-OR^{34}$ or any group readily derivable from it, and each R^{34} is independently hydrocarbyl or substituted hydrocarbyl, and

repeat units derived from one or more alpha-olefins of formulas $H_2C=CH\text{-}(CH_2)_t\text{-}H$ and/or $H_2C=CH\text{-}R^{75}\text{-}G$, wherein t is an integer of 1 to 20, R^{75} is alkylene or substituted alkylene, and G is an inert functional group.